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OXYGEN TRANSFER TO ETHYLENE CATALYZED BY THE AG(110) SURFACE

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types of adsorbed molecular and atomic oxygen has been studied. It is pointed out that the active oxygen transfer species can be an atomic oxygen bound to a silver atom on the surface--an oxo-silver type of complex. The transfer of the oxygen atom from this oxo-silver species to ethylene takes place by an initial interaction of the oxygen with one of the carbons in ethylene. This particular transfer, as well as several from other types of both molecular and atomic adsorbed oxygen are discussed in relation to experimental results and also in relation to the epoxidation of alkenes catalyzed by molecular complexes. The influence of chlorine on the adsorbed oxygen has also been studied.

**OXYGEN TRANSFER TO ETHYLENE
CATALYZED BY THE AG(110) SURFACE⁺**

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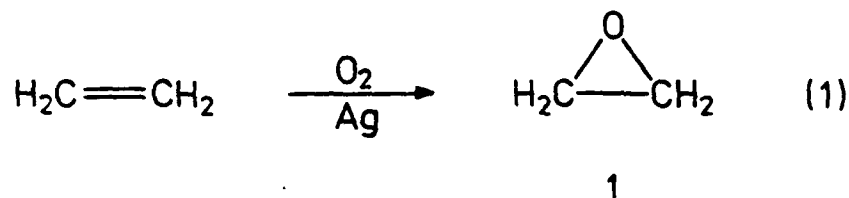
⁺Dedicated to our friend Richard Netter on the occasion of his 70th birthday.



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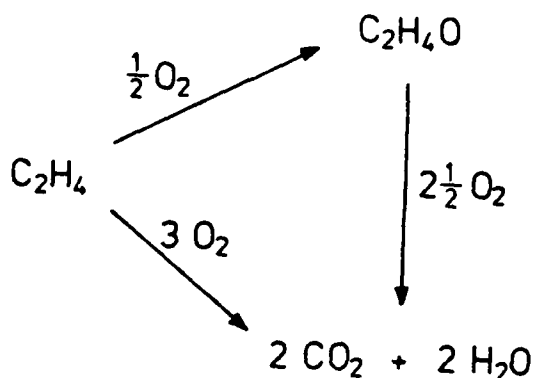
Abstract. - The silver surface catalyzed epoxidation of ethylene using molecular oxygen as an oxygen donor has been studied using extended Hückel calculations. Five types of adsorbed molecular oxygen on an Ag(110) surface have been considered, an end-on adsorption on top of silver, a peroxidic adsorbed molecular oxygen, both on a silver atom on the surface or bound to one in the second layer, and finally molecular oxygen bridging between two silver atoms in the (110) and the (001) direction. For atomic adsorbed oxygen four types of geometries have been considered: two adsorption geometries on top of a silver atom, one on the surface and one in the second layer, and two bridging positions, one between two silver atoms in the (110) direction and the other in the (001) direction. The calculations indicate that the most probable adsorption sites for molecular oxygen are end-on or bridging between two silver atoms in the (110) or (001) directions; for atomically adsorbed oxygen the adsorption on top of a silver atom on the surface, or bridging between two silver atoms in the (110) direction, are favored. Transfer of the oxygen atom from some of the different types of adsorbed molecular and atomic oxygen has been studied. It is pointed out that the active oxygen transfer species can be an atomic oxygen bound to a silver atom on the surface - an oxo-silver type of complex. The transfer of the oxygen atom from this oxo-silver species to ethylene takes place by an initial interaction of the oxygen with one of the carbons in ethylene. This particular transfer, as well as several from other types of both molecular and atomic adsorbed oxygen are discussed in relation to experimental results and also in relation to the epoxidation of alkenes catalyzed by molecular complexes. The influence of chlorine on the adsorbed oxygen has also been studied.

The transfer of an oxygen atom from a silver surface to ethylene leading to ethylene oxide, 1 (Equation 1) is an important reaction in industry - a several-billion dollar per year process.¹ The reaction



also serves as a challenge to the academic field, as the different steps involved in the reaction path are not resolved, in spite of extensive investigations.²

The oxidation of ethylene to ethylene oxide as outlined in (Equation 1) is not the only reaction that occurs when ethylene and oxygen are exposed to a silver surface. Scheme 1 illustrates the dominant reaction paths in ethylene epoxidation catalyzed by a silver surface. Besides the



Scheme 1

epoxidation reaction, combustion of ethylene or ethylene oxide to carbon dioxide and water is also observed.^{2a-d} The selectivity of the reaction (defined as the number of moles of ethylene oxide produced divided by the total ethylene reacted) has been found to be about 45% on clean silver catalysts.³ However, in the presence of either electronegative moderators such as chlorine or the electropositive alkali and alkaline earth metals the selectivity can be increased to 75-87%.²

The use of oxygen on silver surfaces for epoxidation is a unique reaction only for ethylene.^{2,4} Other alkenes as substrates lead to low yields of the corresponding epoxides and little use of silver catalysis has been made for other alkenes.

The silver surface catalyzed epoxidation of ethylene can be considered as a two-step process: first, an activation of molecular oxygen for the oxygen donation step followed by the transfer of an oxygen atom to ethylene. To obtain an understanding of the mechanism of ethylene epoxidation catalyzed by silver surfaces, one is then faced with the following questions: (i) how is molecular oxygen adsorbed on a silver surface, (ii) what is nature of the oxygen which is transferred to the ethylene and (iii) how is the oxygen transferred to the ethylene? Our purpose in the following work will then be to address these questions.

Let us first briefly review some of the experimental results relevant to the analysis presented here. Many surface science studies, particularly on the Ag(110) face, have focused on identifying the oxygen species directly responsible for epoxidation. Three types of oxygen have been observed when molecular oxygen is exposed to an Ag(110) surface: molecular, atomic and subsurface oxygen.²

High-resolution electron energy loss spectroscopy (HREELS) has been used for the identification and characterization of the molecular oxygen species on the Ag(110) surface.^{2d,5} The molecular nature of some of the adsorbed oxygen has also been verified using temperature-desorption experiments with a mixture of $^{16}\text{O}_2$ and $^{18}\text{O}_2$, in which no scrambling was observed below 170°K.^{5,6} X-ray photoelectron spectroscopy (XPS) of molecular oxygen on Ag(110) shows only a single peak, which leads to the conclusion that the oxygen molecules lie flat on the surface, since end-on adsorption would have produced two O(1s) photoelectron peaks.^{7,8}

Molecular orbital cluster calculations of molecular oxygen on Ag(110) revealed two reasonable structures for molecular oxygen, both lying flat on the surface. For one the oxygen molecule is parallel to the direction of the groove, and for other it is located perpendicular to the groove with a preference for the latter.⁹ Recent studies show that the primary, and hence most stable, form of adsorbed molecular oxygen on Ag(110) is with the O-O axis parallel to the plane of the surface with the O-O bond vector along the (110) direction.¹⁰ It should also be noted that a location of molecular oxygen perpendicular to the groove is in accordance with the orientation proposed on basis of electron-stimulated desorption work.¹¹

Atomic oxygen can be formed by dissociative cleavage of molecular oxygen on the silver surface. Atomic oxygen on the (110) surface has been identified by several different techniques.^{2c,d} Low-energy electron diffraction investigations and ion scattering experiments have indicated that oxygen atoms are adsorbed in the grooves of the (110) surface,¹² but it has also been proposed that oxygen can be absorbed in other ways.^{8,13} A few theoretical calculations have also been performed on atomic oxygen bound to silver clusters.¹⁴

The third type of oxygen suggested to be present on a silver surface is subsurface oxygen. By its very nature a detailed characterization of such a species by surface-specific techniques is difficult. Nevertheless its present has been verified by several groups.^{5,15}

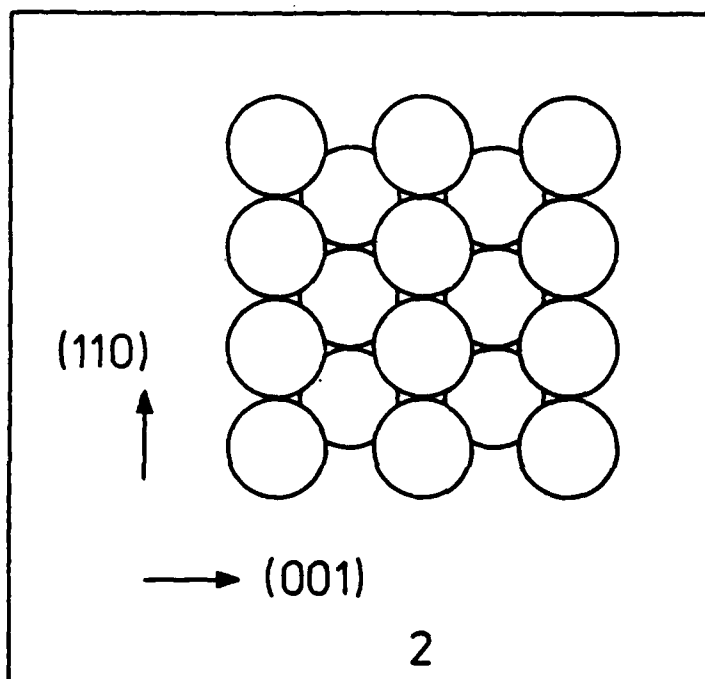
As to the oxygen transfer step, there has been a great debate about the nature of the species involved - molecular vs atomic oxygen.¹⁶ If it is assumed that only molecularly adsorbed oxy-

gen can give epoxide upon reaction with ethylene and that the remaining oxygen atoms cannot recombine on the surface, six oxygen molecules can produce six molecules of ethylene oxide. Because only one oxygen atom per oxygen molecule is incorporated into epoxide, six oxygen atoms will remain adsorbed onto the silver surface. As the reaction can continue "indefinitely", these oxygen atoms must be removed so as not to block the surface. More reactant ethylene will have to be used to remove atomic oxygen in a non-selective complete combustion reaction. Six oxygen atoms are needed for the total oxidation of ethylene (see Scheme 1). These arguments lead to the prediction of a maximum initial selectivity of 6/7, if molecular oxygen provides the reaction path to the epoxide. Few experimental studies have found selectivities larger than 6/7, which is one of the main reasons why this mechanism has found wide support.² Further evidence for a mechanism involving a peroxo species comes from IR studies of the interaction of adsorbed oxygen with ethylene, in which bands corresponding to a surface peroxo species $\text{H}_2\text{C}-\text{CH}_2-\text{O}-\text{O}-\text{Ag}_{\text{surf}}$ have been assigned.¹⁷

The case for the involvement of atomic oxygen in the epoxidation step arises from several types of experimental studies.² It has been shown that it is weakly adsorbed oxygen which yields the epoxide,^{2d,18} and that this weakly adsorbed oxygen is found for $\text{O}/\text{Ag} > 0.5$.¹⁹ Furthermore it has been shown that epoxide is formed in the reaction of ethylene with AgO .^{18a} Oxygen labeling experiments have also demonstrated that atomic oxygen on the surface can be incorporated into the epoxide.^{2d, 20}

The epoxidation of ethylene catalyzed by a silver surface with molecular oxygen as the oxidant is not stereoselective. Epoxidation of *cis*-1,2-dideuteroethylene leads to a substantial amount of the *trans*-epoxide, and the corresponding *trans*-alkene produces some *cis*-epoxide.²¹ In one study, about 70% retention^{21a} of the original conformation was found in the product epoxide, whereas others have observed that the epoxide products are nearly equilibrated.^{21b,c}

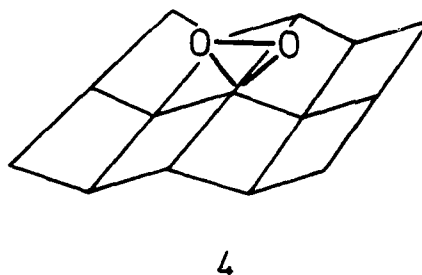
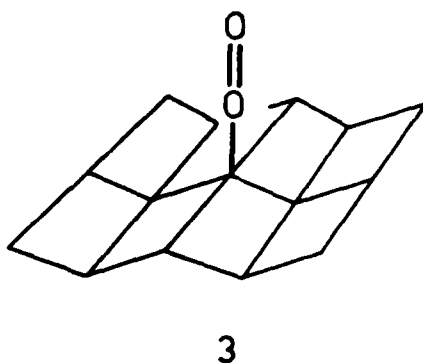
In the present study we will try to elucidate how molecular and atomic oxygen can be adsorbed onto a silver surface in order to determine the electronic nature of the adsorbed species, and to examine how the oxygen transfer step to ethylene can take place. Also, we will consider the influence of moderators, such as chlorine, on the electronic nature of the oxygen which is transferred to the ethylene. For these purposes we will make use of extended Hückel calculations and the two-dimensional character of the system via the tight-binding approximation.²² As the $\text{Ag}(110)$ surface shown in 2 has been shown to be a good model for the real catalyst²³ we have chosen this type of surface for the present study.

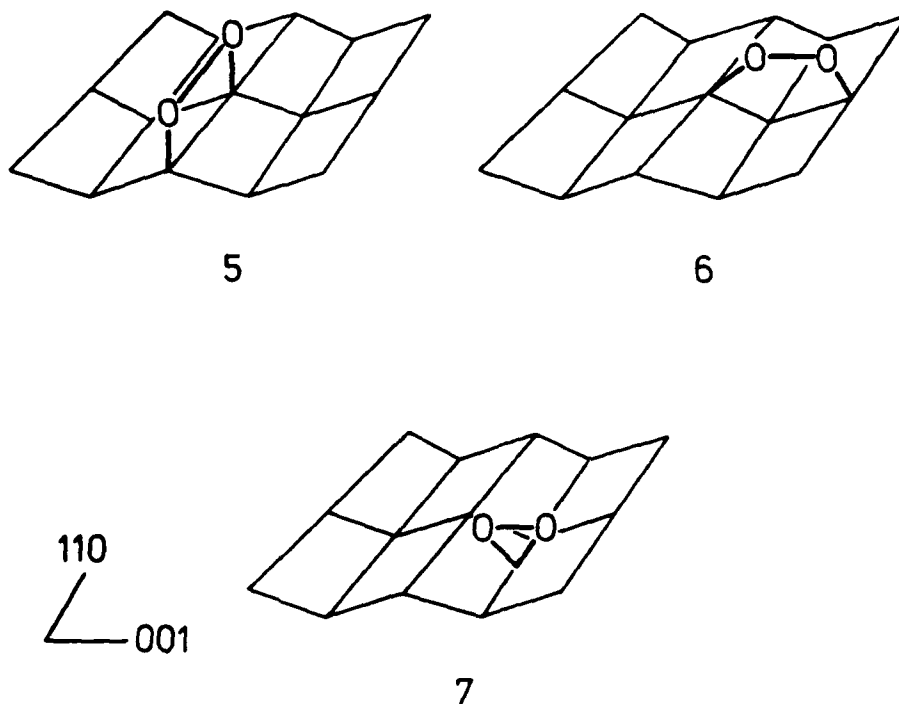


During the writing of this paper Carter and Goddard published a paper concerning the energies involved in the silver-catalyzed epoxidation of alkenes.²⁴ Based on the study of the interaction of atomic and molecular oxygen with a silver cluster they proposed that a surface atomic oxygen is the active oxygen species for forming the epoxide.²⁴

Adsorption of molecular oxygen on Ag(110).

For the adsorption of molecular oxygen on Ag(110) we have chosen to study five binding types: end-on, 3, side on with molecular oxygen bound to one silver atom, 4, bridging between two silver atoms, 5, 6 and finally molecular oxygen bound to one silver atom in the second layer, 7.





Before proceeding to the adsorption of molecular oxygen to the Ag(110) surface let us start with the calculations of the density of states (DOS) for Ag(110).²⁵ Figure 1 shows the total

Figure 1 here

DOS for the system using 3 layers of silver atoms. With the parameters used here the Fermi level has been calculated to -10.69 eV. The d-band is spread out over 2 eV from about -14 to -16 eV; the s molecular orbitals spread out on the vacuum side on the d-band.

Let us start with the end-on adsorption of molecular oxygen, 3; besides the linear approach shown in 3, the oxygen might also be bent. Figure 2 shows the change in energy for 3 as a function of the bending angle, θ . It appears from Figure 2 that the end-on

Figure 2 here

adsorbed molecular oxygen exhibits a weak preference for being bent. The minimum in energy for 3 is found for $\theta=130^\circ$ which is in agreement with the structure found for several mononu-

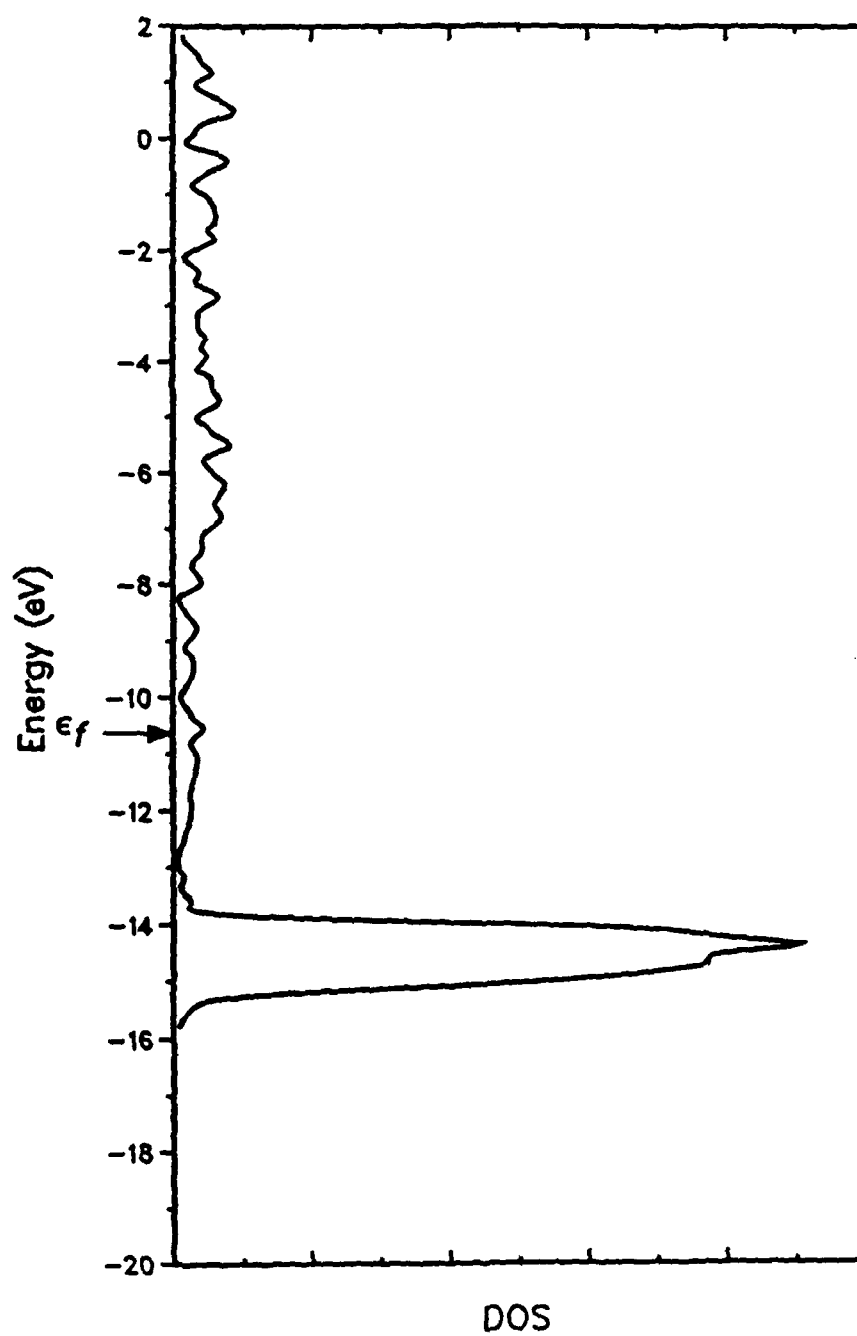


Figure 1. The total density of states (DOS) for Ag(110).

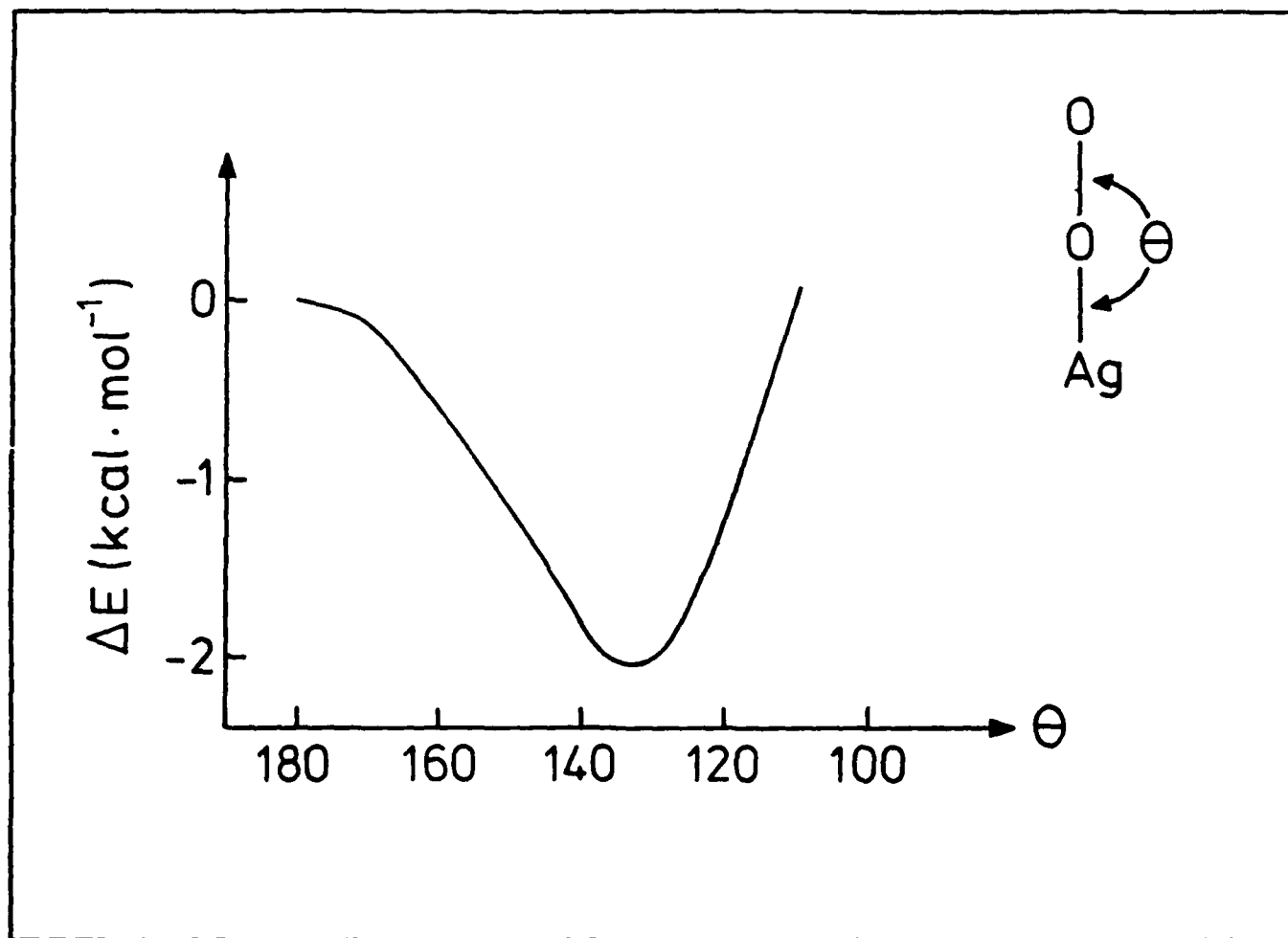


Figure 2. The change in energy for **3** as a function of the bending angle, θ .

clear transition metal superoxo complexes.^{2b} There is no preferred orientation of the bent oxygen relative to the silver surface.

The binding energy and overlap populations for molecular oxygen to the Ag(110) surface, and a model cluster surface, for the different approaches shown in 3-7 are given in Table 1. The results in the parentheses refer to the cluster calculations containing 22 silver atoms, 9 in the surface layer, 4 and 9 silver atoms in the second and third, respectively. The "a" geometries to an orientation of molecular oxygen along the (001) axis and the "b" geometries to an orientation along the (110) axis. It appears from Table 1 that the binding energy for the perpendicular end-on coordination of molecular oxygen to the Ag(110) surface and the model cluster surface are more or less identical, and similar results are also found for the other binding approaches. Upon end-on

Table 1 here

adsorption of molecular oxygen to the Ag(110) surface (with $\theta=130^\circ$), the overlap population between the oxygens decreases from 0.817 to 0.433. The bond character changes roughly from double to single. The orbitals leading to interaction can be traced to a combination of s and d_{z^2} on silver and the π^* of molecular oxygen shown in 8.

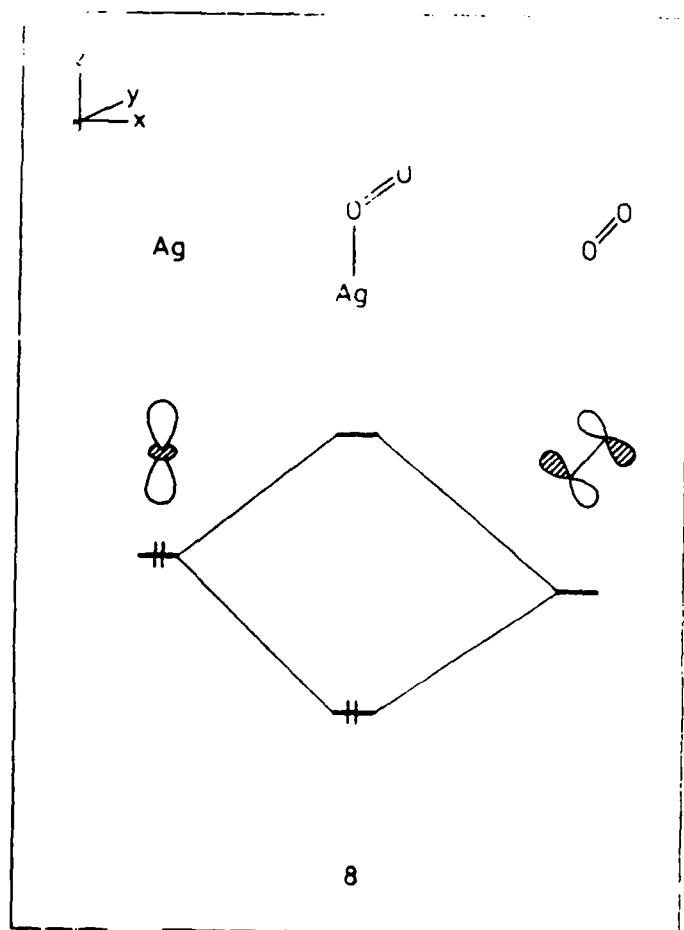


TABLE 1 Binding energies, Fermi levels, Ag-O and O-O overlap populations for Ag(110), O₂ and the different types of adsorbed molecular oxygen, 3-7. Numbers in parentheses refer to cluster calculations.

	Binding energy ^a (eV)	ϵ_F (eV)	Overlap population Ag-O	Overlap population O=O
Ag(110)	-	-10.62	-	-
O ₂	-	-	-	0.817
<u>3</u> ($\theta = 130^\circ$)	5.12 (5.09)	-11.02	0.289 (0.279)	0.433 (0.434)
<u>4a</u>	4.57 (4.74)	-11.02	0.085 (0.090)	0.442 (0.447)
<u>4b</u>	4.49 (4.52)	-11.01	0.083 (0.084)	0.442 (0.443)
<u>5</u>	5.43 (5.21)	-10.99	0.128	0.452 (0.453)
<u>6a</u>	5.16 (5.28)	-10.90	0.240 (0.236)	0.445 (0.443)
<u>6b</u>	3.11 (2.77)	-10.69	0.035 (0.058)	0.449 (0.446)
<u>7a</u>	3.74 (3.13)	-10.59	0.208 (0.178)	0.457 (0.458)
<u>7b</u>	3.52 (3.15)	-10.72	0.141 (0.143)	0.463 (0.467)

^aBinding energy = E(Ag(110)) - E(O₂ adsorbed on Ag(110)).

It turns out that the antibonding combination of the interaction shown in 8 is located below the Fermi level of the silver surface. This antibonding combination will then be populated with electrons from the surface. The Ag-O antibonding interaction is readable from the crystal orbital overlap population (COOP) curve²⁶ shown as the full line in Figure 3b; the antibonding character appears at about -13 eV. Figure 3 shows the total DOS for 3 with the

Figure 3 here

contribution from molecular oxygen as the shaded area (a) and the O-O and Ag-O COOP curves (b).

The end-on adsorption of molecular oxygen gives rise to two new DOS features, one split peak located at -16 eV below the d-block of the silver surface and one at about -13.3 eV above the d-block. From the O-O COOP curve (dotted line in Figure 3b) the latter is seen to be antibonding, thus assigned to the π_{O-O}^* orbital, and the former, being O-O bonding, is mainly derived from the π_{O-O} orbital. The two π peaks are involved in Ag-O bonding as seen from the Ag-O COOP (full line in Figure 3b). The end-on adsorption leads to net transfer of 1.71 electrons from the silver surface to the molecular oxygen fragment with 1.02 electrons located at the terminal oxygen.

Let us now continue with the other approaches of molecular oxygen to Ag(110), 4-7. It appears from Table 1 that the largest binding energy is found for molecular oxygen bound to two silver atoms in the same row, 5. Slightly less favorable is the molecular oxygen bound to two silver atoms in two different rows, i.e. across the grooves, 6a. These three types of adsorption are more than 0.5 eV more stable than the others studied, so we will concentrate our attention on 5 and 6a. The orientation of molecular oxygen in 5, parallel to surface along the (110) axis is in agreement with the results obtained by a near-edge X-ray adsorption fine structure study.^{10a} A previous molecular orbital cluster study of molecular oxygen on Ag (110) gave a preference for the geometries such as 6a,⁹ which is also in accordance with some experimental results.¹⁰ It should also be mentioned that similar binding of molecular oxygen to two transition metals has been observed in several binuclear transition metal complexes.²⁷

The primary interaction which produces the chemisorptive bond in 5 is outlined in 9. The

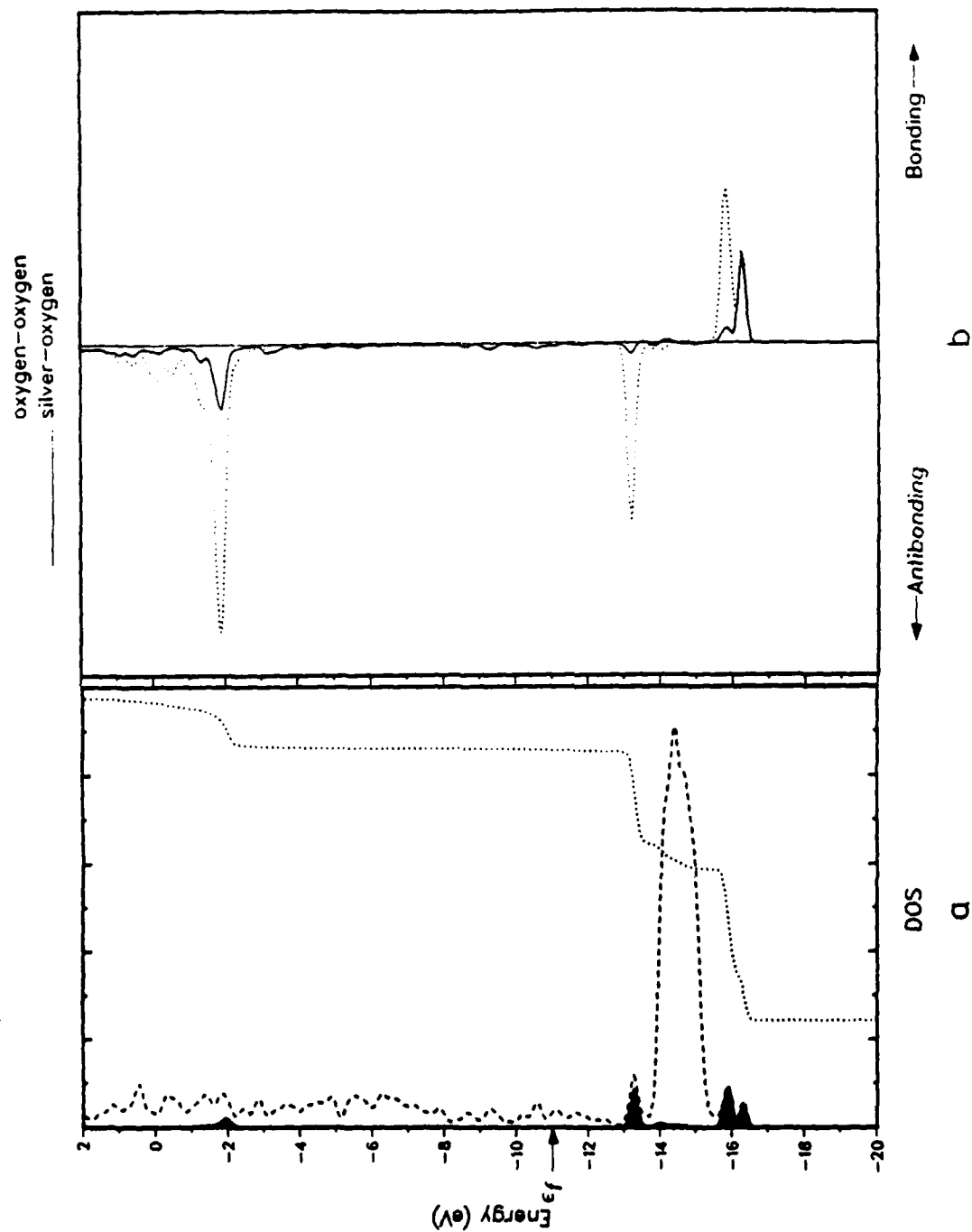
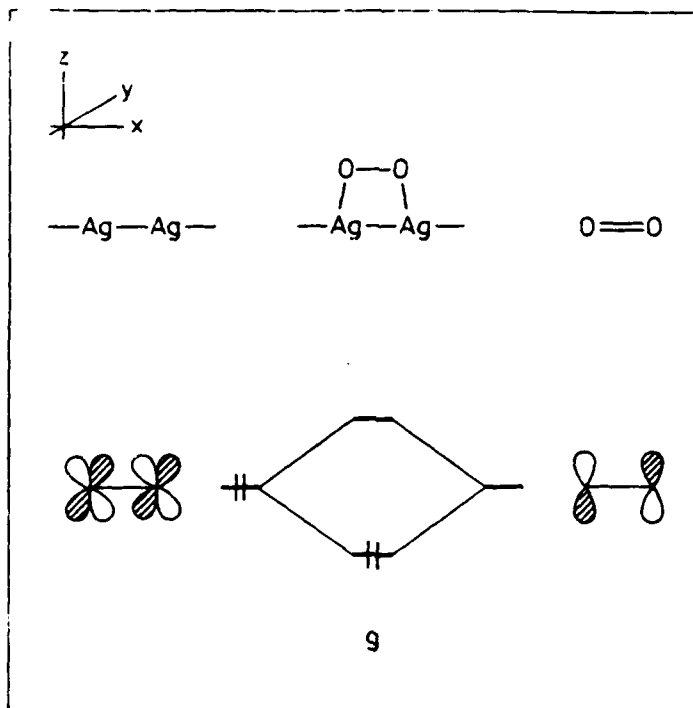


Figure 3. (a) The total DOS for 2; the contribution from molecular oxygen is shown as the shaded area. The dotted line is the integration of the contribution from molecular oxygen. (b) The crystal orbital overlap population (COOP) curves for the oxygen-oxygen bond (dotted line) and the silver-oxygen bond (full line).



interaction takes place between d_{xz} at silver and the π^* of oxygen, leading to a population of both bonding and antibonding combinations shown in 9, because the latter is again located below the Fermi level of the surface. The contribution of molecular oxygen in 5 to the total DOS and the O-O and Ag-O COOP curves are shown in Figure 4. The curves in Figure 3a and 3b and those shown in Figure 4 are more or less alike; the only difference for the DOS curves is that the lower part of the oxygen contribution to the total DOS in Figure 4a is located about 0.5 eV lower in energy compared with Figure 3a. The difference between the

Figure 4 here

COOP curves of 3 and 5 is that the antibonding Ag-O part located at about -13.3 eV in Figure 3b now has changed to a bonding one in Figure 4b at about -14.5 eV.

Moving from an adsorption of molecular oxygen to two silver atoms in the same row (5) to adsorption of molecular oxygen in two different rows (6a) does not change DOS and COOPs curves significantly from those shown in Figure 4. The trends are the same; the relevant curves are not shown here. Both adsorption types, 5 and 6a lead to a net transfer of 1.50 electrons from the silver surface to molecular oxygen.

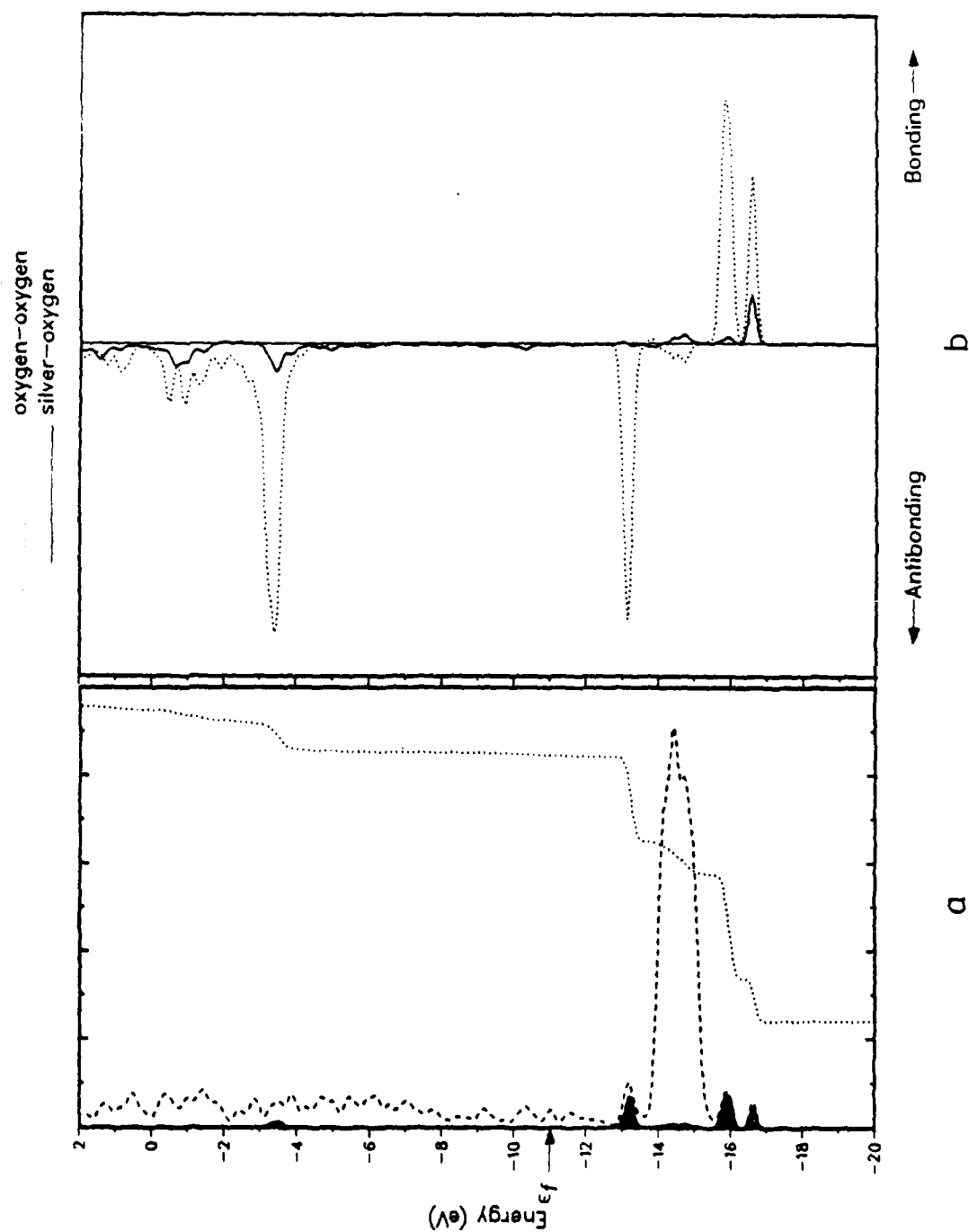
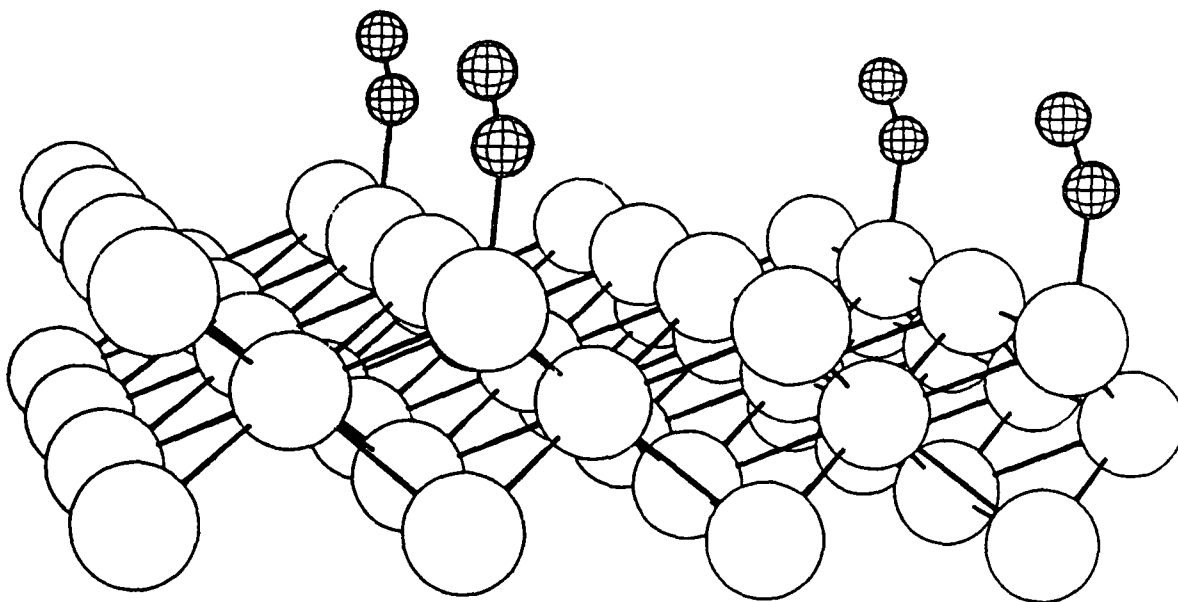
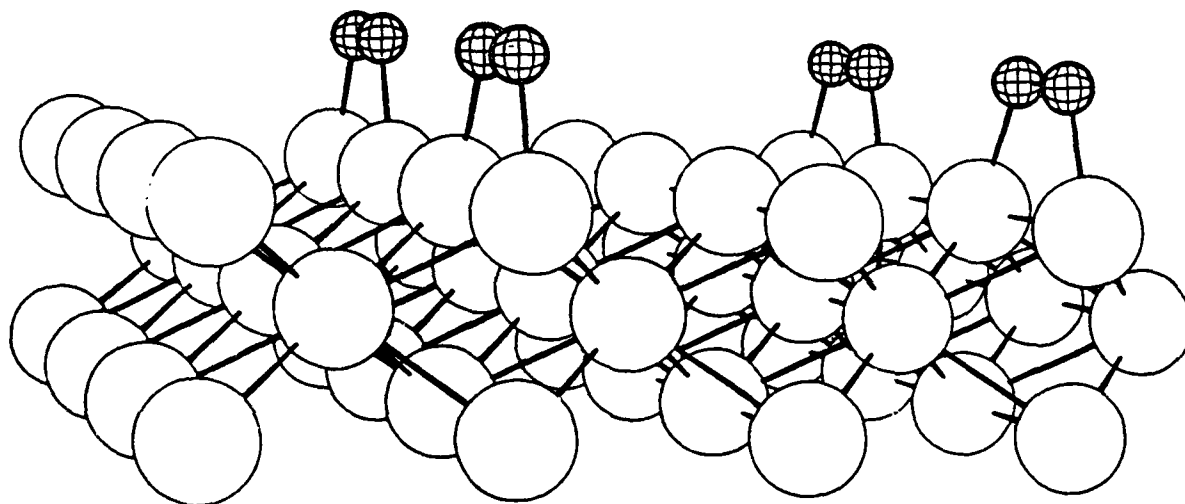


Figure 4. (a) The total DOS for ZnO; the contribution from molecular oxygen is shown as the shaded area. The dotted line is the integration of the contribution from atomic oxygen. (b) The COOP curves for the oxygen-oxygen bond (dotted line) and the silver-oxygen bond (full line).

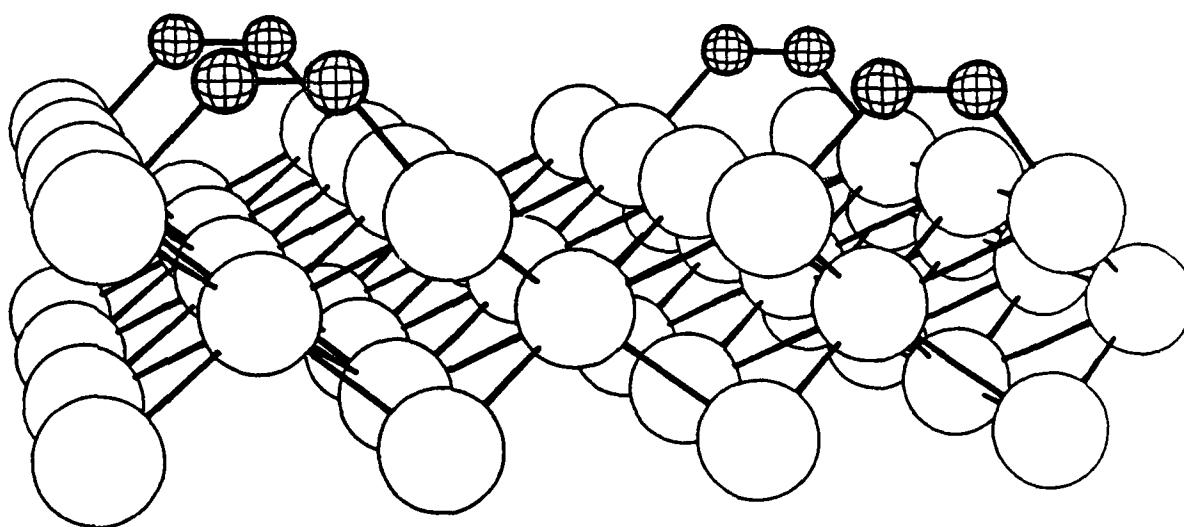
The present results seem to favor 3, 5 and 6a from a binding energy point of view as the most probable adsorption geometries of molecular oxygen to Ag (110), although the difference is not so substantial as to exclude the others. If we take both the binding energy and Ag-O overlap population into account, a slight preference for 6a seems to be indicated (the Ag-O overlap has to be multiplied with two as the oxygen molecule is bound to two silver atoms). This is also the geometry which is supported by experimental investigations¹¹ and molecular orbital cluster calculations.⁹

A more detailed picture of the three preferred adsorption geometries is shown in 10, 11, and 12 (the oxygens are lined).





11



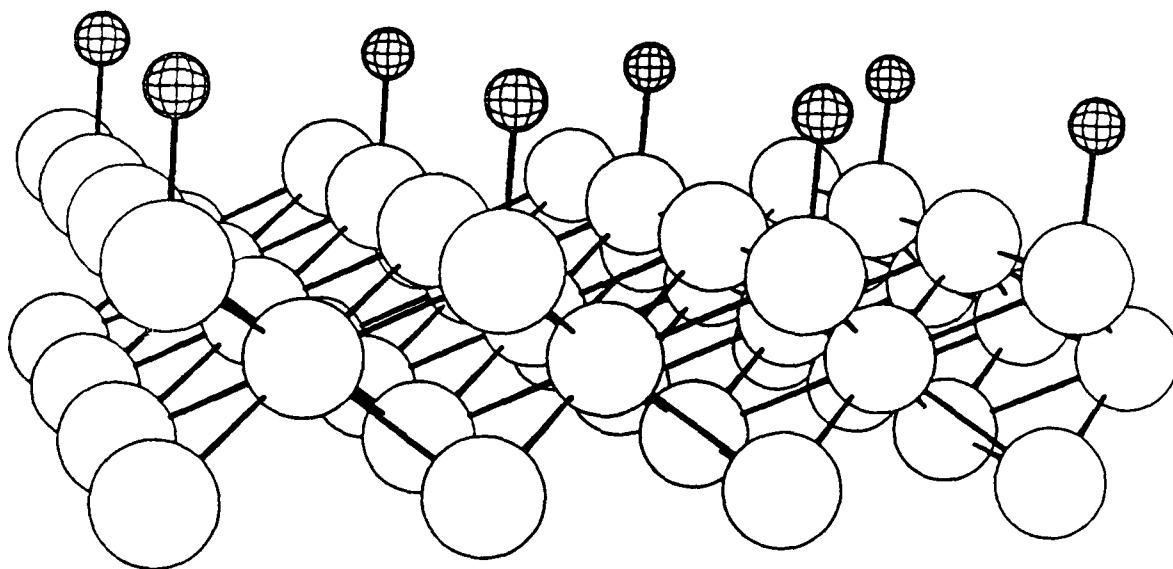
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The net charge of the adsorbed molecular oxygen has in all cases been found to be between -1.50 to -1.71 . Based on the low O-O stretching vibration found for adsorbed molecular oxygen on Ag(110) in comparison with other molecular oxygen reference compounds of varying formal charge⁵, the formal charge of the adsorbed molecular oxygen has been extrapolated to -1.7 . This is in good agreement with our calculated formal charge, but this should also be expected because of back-donation of electrons from the silver surface to the π^* -antibonding orbitals. The latter are below the Ag Fermi level, and so are mostly occupied.

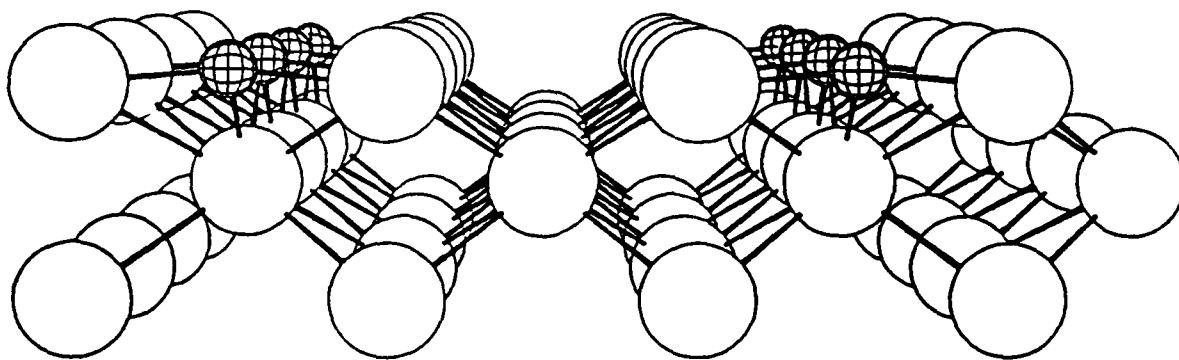
The end-on coordinated molecular oxygen, 3 should, by XPS, give rise to two peaks for the two different O(1s) electrons. Experimentally only one peak is found,⁷ which might make 10 less likely than 11 and 12, as the oxygens in the two latter modes are equivalent. But we will not exclude 10 as a possible model for the active surface species on basis of this result.

Adsorption of atomic oxygen on Ag(110).

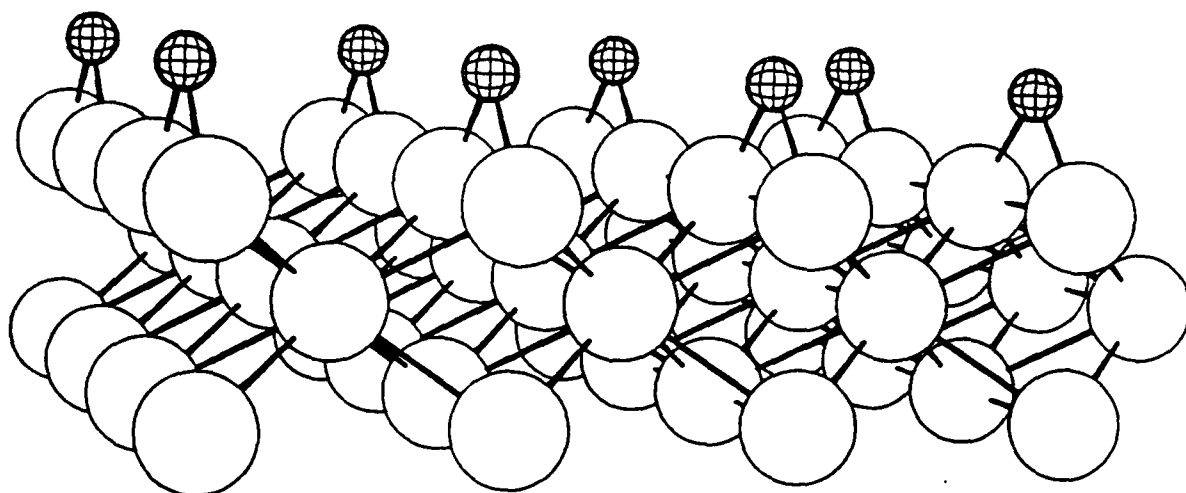
For the adsorption of atomic oxygen on Ag(110) we have chosen to study four binding types: an oxo-silver species, 13, two bridging species, 14 across, and 15, along the grooves, and oxygen bound in the grooves over a silver atom in the second layer, 16 (the oxygens are lined).



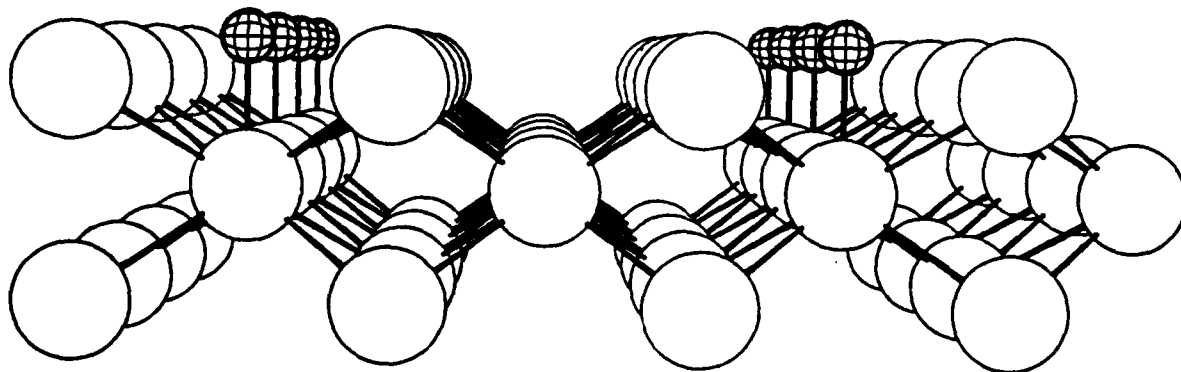
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14



15



16

According to several investigations molecularly adsorbed oxygen on Ag (110) dissociates into atomic oxygen above 170°K.⁸ Considering the population of the π^* antibonding orbitals in chemisorbed molecular oxygen this is not surprising. The binding energies and overlap populations for two atomic oxygens per unit cell, for the different approaches shown in 13-16, are given in Table 2. The results in the brackets refer to cluster calculations.

Table 2 here

Again the trends for binding energies for the two atomic oxygens for the surface and cluster calculations are approximately the same with 13 and 15 being a few eV more stable than 14 and 16.

All the calculations have been performed with a Ag-O distance of 2.1 Å. The structure shown in 13 can be considered as an AgO species, whereas the one shown in 15 is Ag₂O-like.²⁸ The location of oxygens in 14 and 16 is in the grooves. The two latter types of atomic oxygen adsorption might be those which are referred to as subsurface oxygen.^{5,15}

The Ag-O overlap population in 13 is calculated to 0.280; 0.233 in 14 between oxygen and each silver in the surface; 0.187 in 15 also between oxygen and each silver in the surface, and 0.214 in 16 between oxygen and silver in the second layer.

Based on both the binding-energy and overlap populations our calculations indicate thus 13 and 15 as prime candidates for how atomic oxygen is adsorbed on an Ag (110) surface, whereas if we only take the overlap population into account 13 and 16 should also be considered.

The interaction leading to the Ag-O bond in 13 takes place mainly between the Ag d_{z^2} and s orbitals and the O p_z -orbital. Also, the d_{xz} and d_{yz} orbitals on silver interact with the p_x and p_y orbitals on oxygen. Figure 5 shows the total DOS with the total contribution from the oxygens (5a), the contribution from only the oxygen p_x and p_z orbitals, (5b) and (5c),

Figure 5 here

respectively, and the COOP curve for the silver-oxygen bond (5d).

It appears from Figure 5a that the oxygen p levels are spread over ~2.5 eV region from ~-13.5 eV to -16 eV. The interaction of silver d_{xz} with oxygen p_x creates the oxygen contribution to the DOS shown as the shaded area in Figure 5b (similar for silver d_{yz} with oxygen p_y), which are the π_{Ag-O} and σ_{Ag-O}^* which are located as the lowest and highest part of the

TABLE 2. Binding energies, Fermi levels, Ag-O and O-O overlap populations for Ag(110), O₂ and the different types of adsorbed atomic oxygen 13-16. Numbers in parentheses refer to cluster calculations.

	Binding energy ^a (eV)	ϵ_F (eV)	Overlap population ^b Ag-O
13	12.33 (15.22)	-11.39	0.280 (0.213)
14	10.45 (11.37)	-10.79	0.233 (0.214)
15	12.42 (14.19)	-11.25	0.187 (0.173)
16	10.69 (11.09)	-11.00	0.217 (0.271)

^a Binding energy = $E(\text{Ag}(110)) - E(2\text{xO adsorbed on Ag}(110))$.

^b The overlap population is taken to the nearest silver neighbour.

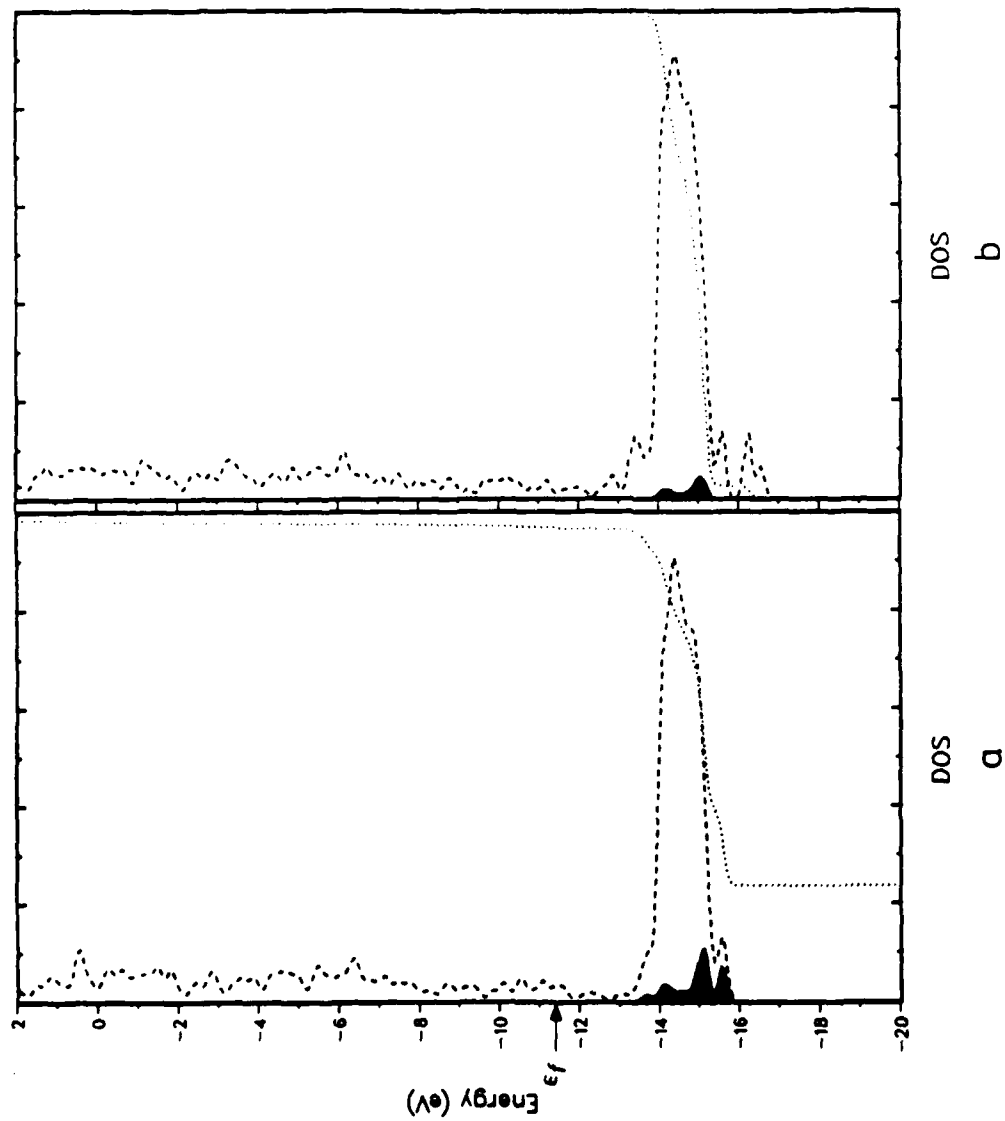
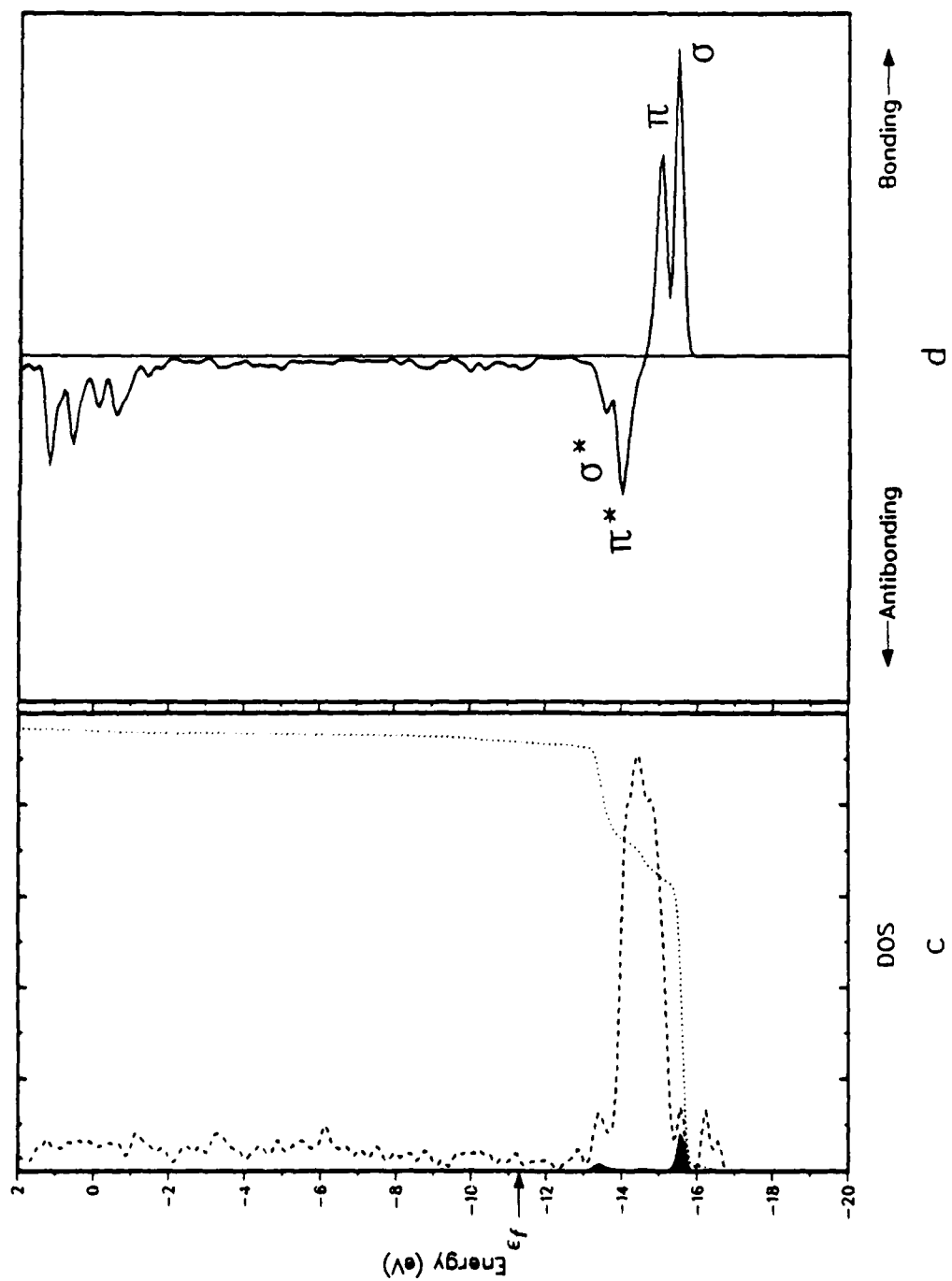


Figure 5. (a) The total DOS for 13; the contribution from atomic oxygen is shown as the shaded area. The dotted line is the integration of the contribution from atomic oxygen.
 (b) The contribution from the oxygen p_x orbital.
 (c) The contribution from the oxygen p_z orbital.
 (d) The COOP curve for the silver-oxo bond.

— silver-oxo bond



oxygen contribution to DOS (Figure 5c). The location of the bonding and antibonding character of the Ag-O bond is seen in Figure 5d. The net charge on oxygen in 13 is calculated as -1.74 , which is the same charge as found on adsorbed molecular oxygen unit. But the "high negative" net charge on oxygen in 13, as well as the charge on the oxygen in the other oxo-silver surface complexes is expected, because all the oxygen orbitals are located below the Fermi level of the silver surface.

The contribution to the DOS for the bridging atomic oxygen, 15, is shown in Figure 6.

Figure 6 here

The oxygen states are localized to three separate levels, one right below and one above -16 eV and one between -13 and -14 eV. The oxygen directly below -16 eV is mainly related to interaction of the oxygens p_x orbital with two silver $d_{x^2-y^2}$ orbitals, and the oxygen contribution to the DOS found right above -16 eV is in a similar way related to the interaction of the oxygen p_y and p_z orbitals with the silver d_{xy} and d_{xz} orbitals, respectively. The Ag-O COOP curves (Figure 6b) show that the interaction between oxygens p_x orbitals and silver $d_{x^2-y^2}$ is responsible for the major part of the binding between these atoms. The total charge on the oxygen is -1.32 .

The contribution from the oxygens to the DOS for 15 is much like the curves shown for 13 in Figure 5a; it is spread out over about 2.5 eV. The COOP curve for the Ag-O bond for 15 does not show the splitting into σ and π bondings and antibonding character as 13 does. The antibonding character between silver and oxygen is located lower in energy in 15 when compared to 13.

Our calculations of adsorbed molecular and atomic oxygen on Ag (110) leave us with several possibilities for the active oxygen donor species on a silver surface: end-on adsorbed molecular oxygen, 10, bridging molecular oxygen, 11 and 12, and both on-top and bridging atomic oxygen, 13 and 15, respectively. As far as bending is concerned, our calculations seem to favor atomic adsorbed oxygen. But strong bonding does not necessarily point the species that is involved in the catalytic act, i.e. in promoting the lowest activation barrier a reaction. We think we must leave open the possibility of either an atomic or a molecular species being active in the catalysis.

The two bridging molecular oxygen species, 11 and 12 are interesting, since by dissociation of the oxygen-oxygen bond, they can lead to the on top adsorbed atomic oxygen, 13. 11 and 12 may then be the precursor adsorbed molecular oxygen species which might give the atomic adsorbed oxygen, 13.

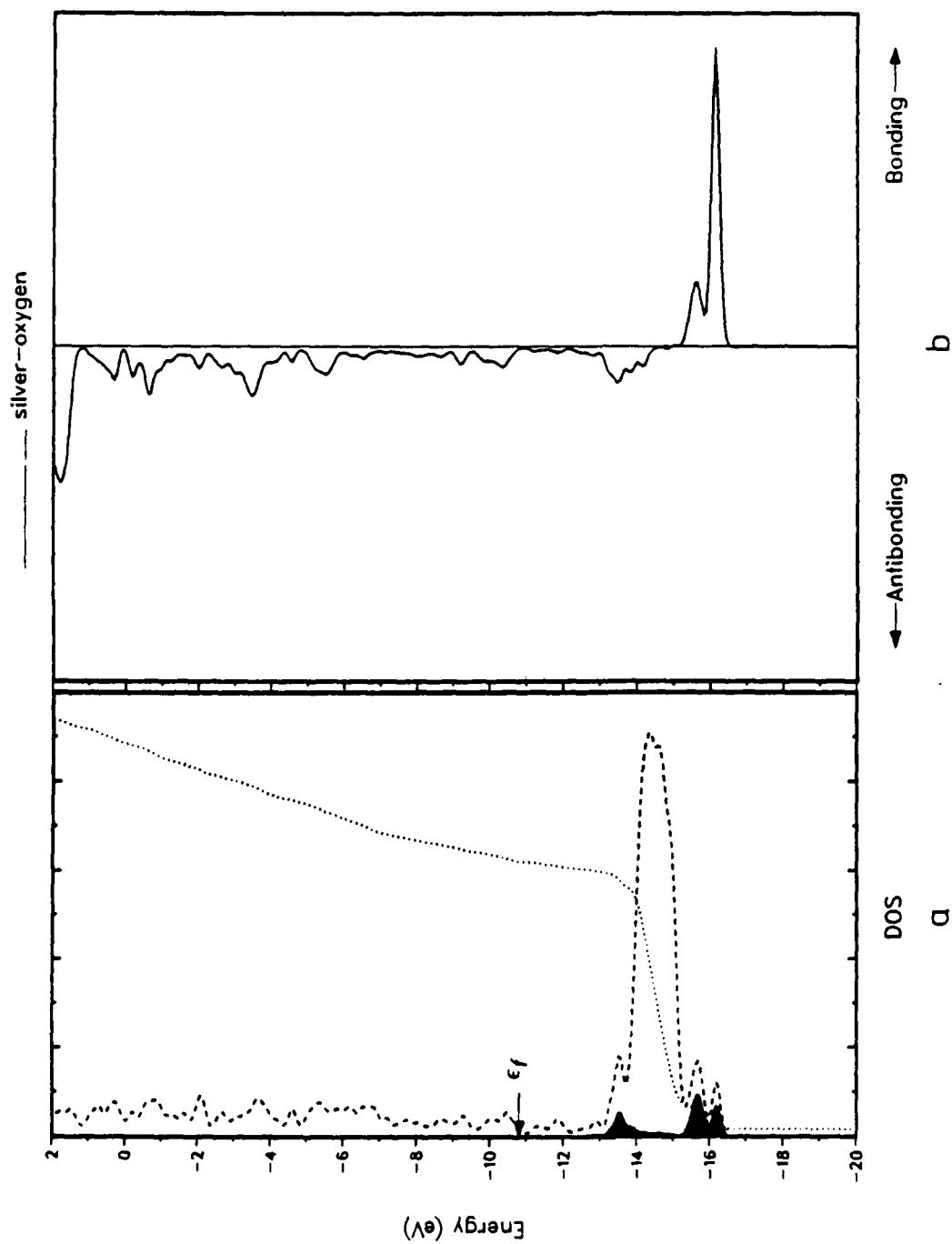
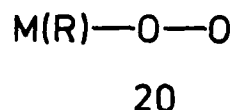
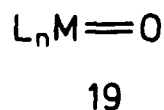
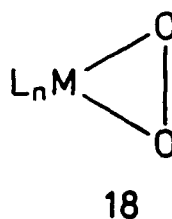
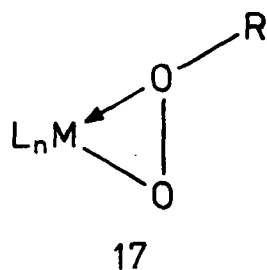


Figure 6. (a) The total DOS for 15; the contribution from atomic oxygen is shown as the shaded area. The dotted line is the integration of the contribution from atomic oxygen. (b) The COOP curve for the silver-oxo bond.

The oxygen transfer step.

Before proceeding to the transfer of the oxygen from the silver surface to the ethylene we find it appropriate to draw attention to the different mechanisms suggested for the epoxidation of alkenes catalyzed by molecular transition metal complexes.^{2e,28} Our intention is to try to build a bridge from what is known about the epoxidation reaction catalyzed by molecular complexes to the epoxidation of ethylene by oxygen on a silver surface.

Three main types of complexes are involved in the transfer of an oxygen atom from the reactive intermediate to an alkene: (i) transition metal peroxide/peroxo complexes, 17, 18, (ii) oxo-transition metal complexes, 19 and (iii) peroxo radicals, 20.^{2e,29-31} The transition metal peroxide (peroxo) complexes are operative in the beginning of the transition metal series, where the transition metal is in its highest oxidation state $-d^0$ making a coordination of the peroxide/peroxo group possible.^{2e} The oxo-transition metal complexes act as catalysts from the middle towards the end of the transition metal series and in some cases side by side with peroxo radicals.^{2e}



Some of the molecular and atomic oxygen species present on the Ag (110) surface are thus comparable to the molecular species, 17-20. As far as we know, molecular species containing

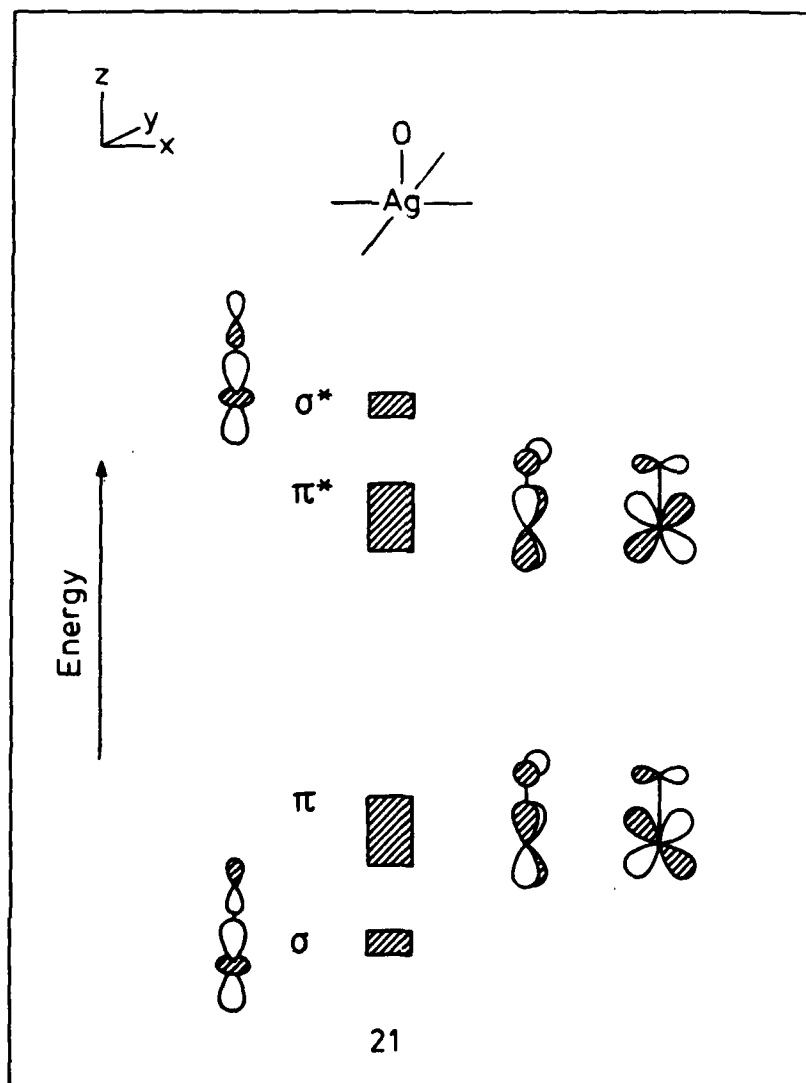
bridging molecular and atomic oxygen (comparable to 11, 12, 14 and 15) are not known to be involved in oxygen transfer to alkenes leading to epoxides.

If we assume that the oxygen species decisive in both molecular and surface epoxidation are similar, we end up with two main candidates for the active surface-oxygen transfer species from our calculations: 10 and 13.

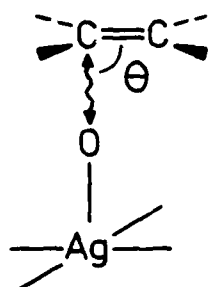
In the molecular systems the oxo-transition metal complexes have in particular been studied with porphyrins^{2e,29,31} and salens^{2e,32} as ligands. The active oxo-transition metal complex is prepared from the transition metal complex and an oxygen donor system. Some of these oxo-transition metal complexes have a property which is comparable to oxygen on a silver surface - they transfer the oxygen atom to an alkene in a non-stereoselective way, as epoxidation of cis-alkenes gives a mixture of both cis- and trans-epoxides.^{2e,29,31,32}

The peroxo-radical complexes are also known from molecular systems; they add to alkenes giving epoxides, but this reaction is often accomplished by side reactions.²⁹

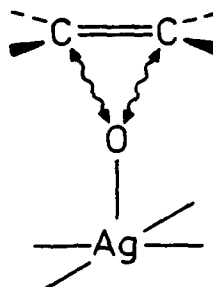
In the following we discuss the oxygen transfer step to ethylene from several types of both molecular and atomic adsorbed oxygen on Ag (110). As a starting point we will use 13 as the active species; the frontier orbitals of the oxo-silver part of 13 are shown in 21.



Given the frontier orbitals of ethylene, π and π^* , two types of interaction between the oxygen in 13 and ethylene are possible. These are shown in 22 (with variable θ) and 23:



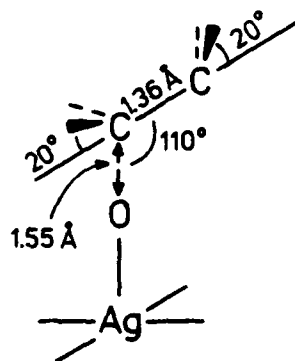
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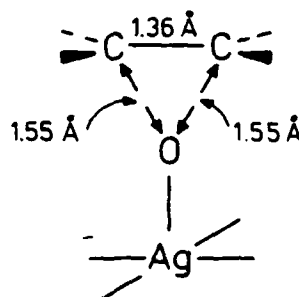
23

The approach of the ethylene to the Ag-O bond depicted in 22 corresponds to interaction of the σ^* Ag-O orbital with the π^* of the ethylene, whereas the approach shown in 23 corresponds to interaction of the π^* Ag-O orbital with the π^* orbital of ethylene. Besides the attractive interaction between high occupied MOs (HOMOs) at oxygen in 13 and the lowest unoccupied MO (LUMO) in ethylene, repulsive interaction between the Ag-O σ^* orbital and the HOMO of ethylene is also observed in 23.

We have calculated the total energy for the two different approaches 24 and 25. The relevant geometries of ethylene relative to the Ag-O fragment are shown below, where the carbon interacting with oxygen in 24 is made nearly tetrahedral:



24



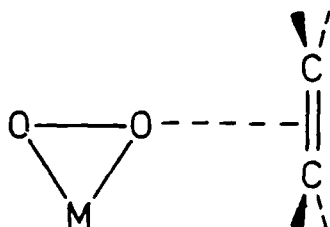
25

Our calculations show that 24 is 7 kcal·mol⁻¹ more stable than 25. Bending the hydrogen up in 25 leads to an even greater destabilization. The overlap population of interest in the two systems are: 24: Ag-O: 0.242; O-C: 0.410; C-C: 0.942 and in 25: Ag-O: 0.252; O-C: 0.367; C-C: 0.804. Without ethylene the Ag-O overlap population is 0.280. It appears from the overlap that the Ag-O bond in 24 is weakened slightly more than in 25 and that the O-C bond in 24 is stronger than in 25. Both C-C overlap populations are reduced significantly compared to ethylene, and correspond approximately to a C-C single bond. With these results favoring the unsymmetric intermediate, 24 the possibility of free rotation around the C-C bond is thus possible. This can allow for the previously mentioned change of the stereochemistry of the alkene during the oxygen transfer step.²¹

Approach of ethylene to the terminal oxygen of the molecular on-top bound species in 10 produces a similar preference for the unsymmetric intermediate with one of the ethylene carbons bound to the oxygen. The energetic and overlap population trends found for the interaction of ethylene with 10 are comparable to those found for the approaches shown in 24 and 25.

One might ask here: Could oxygen transfer from some of the other molecular and atomic adsorbed oxygen species not be possible? So let us here try to discuss the likelihood of oxygen transfer from what we think are less realistic structures of molecular and atomic oxygen, in relation to oxygen transfer to ethylene, on an Ag (110) surface.

Let's turn to the peroxo-like adsorbed molecular oxygen, 4. It has been suggested for the analogous molecular peroxo complexes that the alkene has to approach the oxygen (which is going to be transferred to the alkene) along the oxygen-oxygen bond as shown in 26.^{2e,33} The alkene can

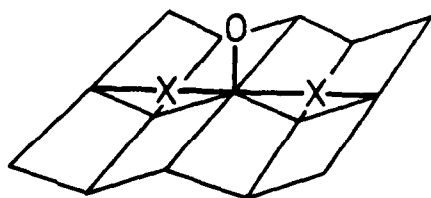


also approach perpendicular to the metal peroxo plane.^{2e,33} It has been observed for instance that peroxo-titanium porphyrins are unreactive towards alkenes,³⁴ whereas titanium peroxide complexes in general are known to be good epoxidation species.^{2e,29} The reason for the unreactive peroxo-titanium porphyrin might be that the alkene cannot approach the peroxo bond as shown in 26, because of steric repulsion between the alkene and the porphyrin ligand,

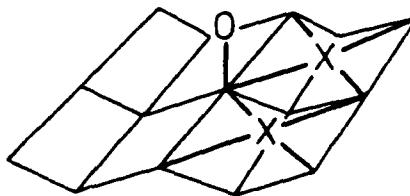
whereas in the titanium peroxide complexes an approach of the alkene along the oxygen-oxygen bond is feasible. If molecular oxygen is present in the form of peroxy or bridging oxygen on a silver surface, the arguments outlined above might indicate that oxygen transfer from these species to ethylene is less probable, particularly when compared with the approach to atomic oxygen shown in 24, because the approach of ethylene to the O-O bond as outlined in 26 will lead to steric repulsion between the silver surface and ethylene. We are thus left with the three atomic adsorbed oxygen types, 14-16 and molecular oxygen, 10. The bridging atomic oxygen, 15, is slightly more strongly bound to the surface than the on top bound atomic oxygen, 13, but can probably very easily be converted to 13 by a movement along the (110) axis. Based on our knowledge of molecular systems we do not think that 15 is the active oxygen species for epoxidation of ethylene, but we can of course not exclude 15 as being present on the silver surface and active in the oxygen transfer step. The two types of adsorbed oxygen in the grooves, 11 and 16 are interesting. In both cases the ethylene has to come very near to the surface to interact with these oxygens. This is probably unrealistic compared with the approach depicted in 24. But as we will be shown in the next section, these adsorptions of oxygen (and chloride) in the grooves of the silver surface might account for the effect of moderators on the reaction course.

A possible model for the effect of moderators (chlorine).

Chlorine has been found to increase the yield of ethylene oxide significantly when added as a moderator during the reaction.² It has also been shown on silver powders that only if the total amount of oxygen atoms adsorbed exceeds half the number of silver surface atoms (i.e. $\theta_o > 0.5$), will the adsorbed oxygen be in a state able to react with ethylene to yield the epoxide. We have studied the effect of the presence of both oxygen and chlorine in the grooves of both 10 and 13. Let us start with the influence of oxygen and chlorine in the grooves of Ag (110) when atomic oxygen is bound to the top of a silver atom. Two types of models have been considered, 27 and 28:



27



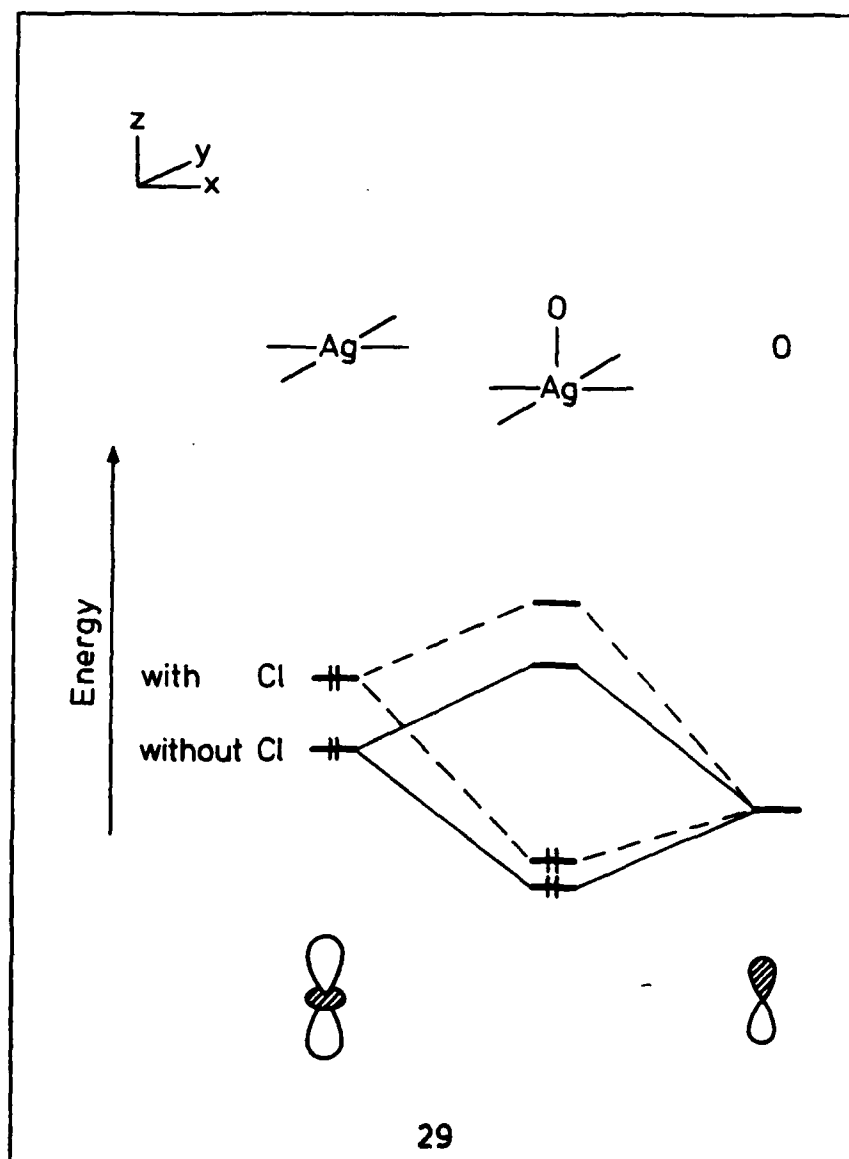
28

X = O, Cl

In 27 X (Cl or O) is bridging between two silver atoms in two different rows, and in 28 X is placed over a silver atom in the second layer. Table 3 shows the change in silver-oxygen overlap with X as shown in 27 and 28

Table 3 here

It appears from the results that the presence of oxygen or chlorine in the grooves of the silver surface leads to a decrease of the Ag-O overlap population. The largest decrease is found for chlorine placed as bridging between two silver atoms in two different rows, 27. Our calculations indicate thus that the Ag-O bond is particularly weakened by the presence of chlorine in the grooves, which makes the oxygen transfer to ethylene easier. Chlorine and oxygen in the grooves push the d-orbitals up in energy relative to the case where no moderator atoms are present. This is shown schematically for the d_{z^2} orbital of silver to the left in 29. The interaction



between the silver d_{z^2} orbital without chlorine present and the oxygen p_z orbital is shown as the full line, and the interaction with chlorine present as the dotted line in 27. It is seen that the bonding level is not perturbed significantly by the interaction, whereas the antibonding level is pushed up in energy when chlorine is present. Figure 7 shows a comparison of the COOP curves for 13 and 27 ($X=Cl$).

Figure 7 here

The increase in energy of the location of the σ_{Ag-O}^* in the presence of chlorine in grooves of the silver surface is easily seen from the dotted line in Figure 7. It appears that this level is pushed up to ~ 13.2 eV from ~ 13.7 eV in 13 (the full line).

We have done the same analysis for end-on adsorbed molecular oxygen, 10, and also here we observe a decrease in Ag-O overlap population, but we see no difference in O-O bonding with or without chlorine. This indicates that the O-O bond in 10 is not activated by the presence of chlorine in the grooves.

With the models used here for the presence of chlorine as moderators in the silver surface catalyzed epoxidation of ethylene we are thus able to explain the effect of chlorine on the reaction course. But one should be aware of that it is a problem in analyzing the effect on the Ag-O bond as presented here, because probably anything attached to that Ag will weaken the Ag-O bond because it uses up some of its bonding capacity.

The halogens make the oxygen in 13 easier to transfer to an ethylene, whereas the oxygen which is going to be transferred in 10 is unaffected by the presence of chlorine. These results seem to favor 13 as the active intermediate in the epoxidation of ethylene catalyzed by a silver surface. It should also be mentioned that the presence of electron-withdrawing groups around the oxo-transition function in the molecular systems increases the reactivity of the oxo-transition metal complex.^{31,35}

Summary

The present study indicates that three different types of adsorbed molecular oxygen on Ag (110) are preferred. These are end-on adsorption on top of a silver atom on the surface and bridging between two silver atoms in the (110) or (001) direction. The calculations do not give a clear preference as to which one is most probable. Molecular oxygen adsorbed as peroxo-like on top of a silver atom on the surface or in the second layer seems to be slightly less favorable. Atomic oxygen appears to have a preference for being adsorbed either on top of a silver atom on the

TABLE 3 The silver-oxo overlap populations for 13, 27 and 28.

	<u>silver-oxygen overlap populations</u>
<u>13</u>	0.280
<u>27</u> (X=O)	0.261
<u>27</u> (X=Cl)	0.222
<u>28</u> (X=O)	0.276
<u>28</u> (X=Cl)	0.259

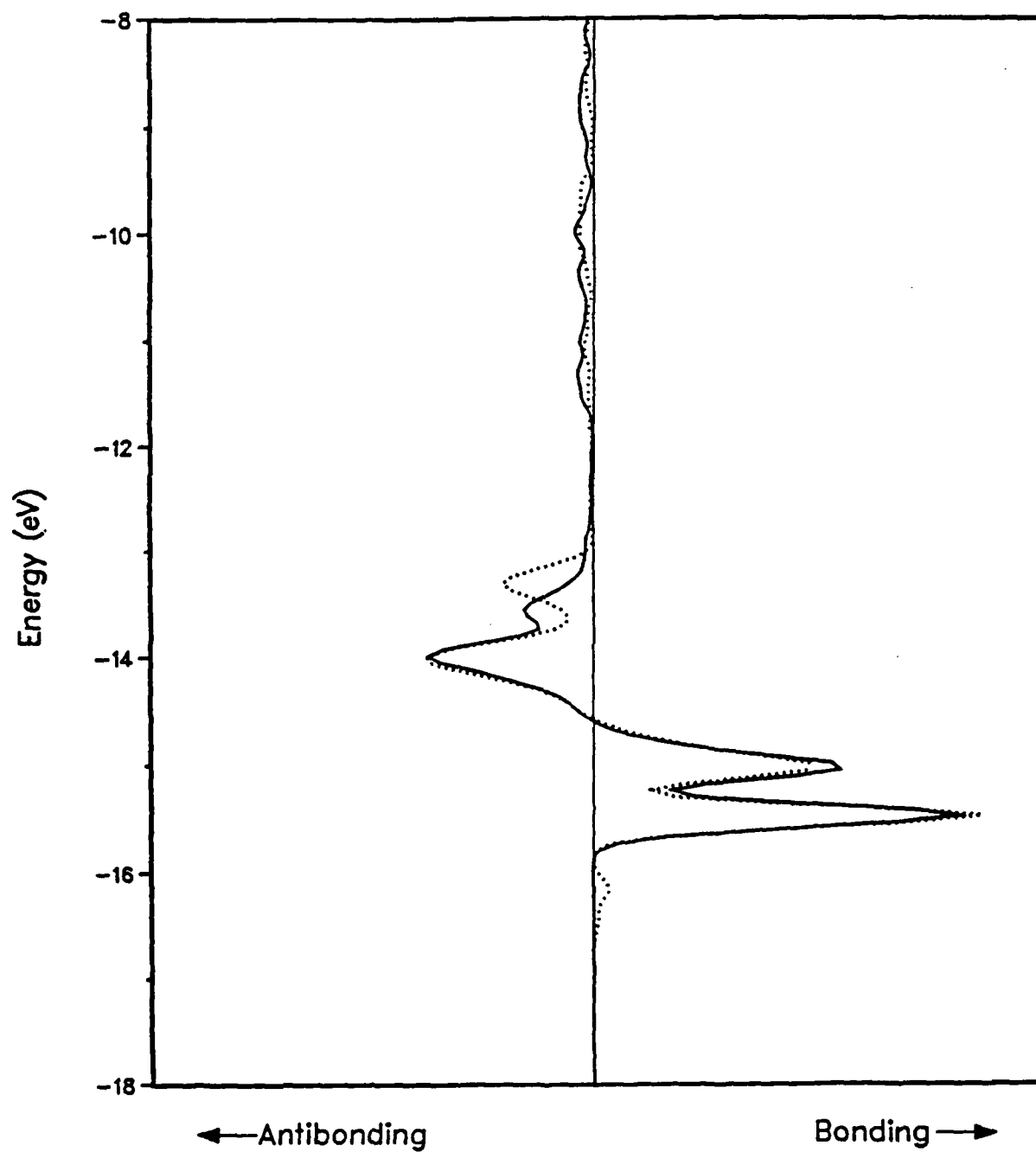


Figure 7. The COOP curves for 13 (full line) and with chlorine as moderator, 27 (dotted line).

surface or between two silver atoms in the (110) direction. Atomic oxygen located in the grooves of the surface is also possible. The adsorption of molecular oxygen to the silver surface leads to filling of the π_{O-O}^* orbitals between silver and oxygen. It is suggested that an oxo-silver species is probably the one which leads to epoxidation of ethylene. The ethylene can approach the oxygen in the oxo-silver species in two different ways, an unsymmetric way be which the oxygen interacts with one of the carbons in ethylene or a symmetric interaction where the oxygen interacts with both carbons. Our calculations prefer for the former. Such an interaction opens up the possibility for free rotation around the carbon-carbon bond in ethylene, leading to a non-stereospecific oxygen transfer step. This is in accordance with the experimental results. The transfer of oxygen from several of the other molecular and atomically adsorbed oxygen species to ethylene is also discussed. The increased yield of ethylene oxide when chlorine is present during the reaction has been suggested to be caused by an adsorption of chloride in the grooves of the silver surface leading to a decrease in the overlap between silver and oxygen, making the oxygen easier to transfer to ethylene.

Appendix

All the calculations have been performed using the extended Hückel method.^{22a} The parameters are listed in Table 4.

Table 4 here

In all the calculations the following bond distances (Å) were used Ag-Ag (110) 2.89, Ag-O 2.12, O-O 1.40, C-C 1.36, C-H 1.08. All surface calculations were of the tight-binding extended Hückel type.²² In all cases 9 k-points were used in the irreducible part of the Brillouin Zone.

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TABLE 4 Extended Hückel parameters

Orbital	$H_{ii}(\text{eV})$	ζ_1^a	ζ_2^a
H 1s	-13.60	1.30	
C 1s	-21.40	1.625	
2p	-11.40	1.625	
O 2s	-32.30	2.275	
2p	-14.80	2.275	
Ag 5s	-11.10	2.244	
5p	-5.80	2.202	
4d	-14.50	6.070(0.55910)	2.6630(0.60476)

^aExponents and coefficients in a double zeta expansion of the metal d orbitals.

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